

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 1 306 013 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**02.05.2003 Bulletin 2003/18**

(51) Int Cl.<sup>7</sup>: **A23G 3/30**

(21) Application number: **01201162.3**

(22) Date of filing: **28.03.2001**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**

Designated Extension States:

**AL LT LV MK RO SI**

(71) Applicant: **Hycail B.V.**

**9804 TG Noordhorn (NL)**

(72) Inventor: **Södergard, Anders**

**9728 WJ Groningen (NL)**

(74) Representative: **Prins, Adrianus Willem et al**

**Vereenigde,**

**Nieuwe Parklaan 97**

**2587 BN Den Haag (NL)**

(54) **Biodegradable gum base**

(57) The invention is directed to a chewing gum, comprising a gum base and at least one other conventional chewing gum component, said chewing gum comprising as gum base at least one branched polymer mainly based on biodegradable and/or hydrolyzable ester groups.

**EP 1 306 013 A1**

## Description

**[0001]** This invention relates to a chewing gum containing a gum base and/or additives from biodegradable resources showing improved chewability with regard to earlier described formulations based on biodegradable polymers. It is known that chewing gum formulations can be made from biodegradable, environmentally more acceptable polymers than the conventional non-biodegradable polymers used as gum base in chewing gums. Examples of this have been described in, for instance, US Pat 5,672,367 and EP O 711 506 A3, where alifatic polyesters were used, and WO99/39588, where bacterial polyhydroxyalkanoates having side chains of C<sub>4</sub> to C<sub>30</sub> were used in chewing gum formulations.

**[0002]** In the present invention, however, the gum base is based on branched or star-shaped polymers with several polyester branches or arms attached to a central polyfunctional compound, thus, surprisingly, resulting in a gum base having improved softness and chewability. Further improvements in the current invention are the use of certain starting compounds or preparation conditions giving the final chewing gum additional functional properties

**[0003]** The present invention relates to a degradable chewing gum, where special properties are achieved by the choice of starting compounds and/or preparation conditions during the synthesis of the polymer or during post-polymerization processing.

**[0004]** The polymers used according to the present invention are branched polymers with several polyester branches or arms polymerized onto a polyfunctional compound with desired properties. A polymer according to the invention can be prepared from the ring-like ester, such as L,L-lactide, D,D-lactide, *rac*-lactide, *meso*-lactide or mixtures thereof, glycolide, trimethylene carbonate, lactones, such as  $\beta$ -propiolactone,  $\delta$ -valerolactone,  $\epsilon$ -caprolactone, or other corresponding cyclic compound like cyclic amides. The polymer can also be prepared by condensation reaction from a hydroxy acid, such as lactic acid, glycolic acid, amino acids or from monomeric units of diols and diacids. Such a polymer can for instance be used in the form of block copolymers, random copolymers, graft-copolymers or as mixtures of two or more homo- and/or copolymers. The invention can be described as a concept where the starting compounds in the polymerization will affect a larger number of different properties, of which some are described below:

1. The initiator determines the structure of the polymer, i.e. the degree of branching, which reflects on the viscoelastic properties of the gum base, which in turn determines the chewing properties of the chewing gum (examples on such compounds are decanol, pentaerythritol, dipentaerythritol).

2. The type of starting materials used can have an impact on other properties related to the performance and appearance of the chewing gum. Examples on such properties are the sweetening effect, compatibility with other ingredients, and taste retention (examples on such compounds are decanol, sorbitol, inositol).

3. The choice of starting material and/or preparation conditions or post-polymerization processing may offer benefits in the view of health aspects for instance by equipping the gum base with for instance antibacterial effect (lactic acid and lactones are known antibacterial substances) or other effects (examples on such compounds are lactones, xylitol, organic acids, hydroxylapatite).

4. The starting material, ways of preparation and processing conditions have a significant impact on the hydrolytic stability of the polymer used in the gum base, which will affect the compostability and enable the removal of undesired chewing gum from, for example, clothes, furniture, streets, and floors. Degradation enhancing compounds can be compounds increasing the hydrophilicity (for instance anhydrides or carboxylic acid compounds) or compounds catalyzing the rate of hydrolysis (for instance amino or amido compounds).

**[0005]** The polyfunctional compounds according to present invention typically contain three or more hydroxyl groups, such as trimethylolethane, trimethylolpropane, butanetriol, phloroglucinol, erythritol, pentaerythritol, or dipentaerythritol. Naturally occurring polyfunctional compounds of sugars of mono-, di-, or trisaccharides of hexoses or pentoses, or maltitol, sorbitol, mannitol, xylitol, inositol, or such, can optionally be used. The polyfunctional compound can be used alone or in any combination with other homo- or polyfunctional compounds. It should, however, be understood that current invention should not be limited to the few polyfunctional compounds mentioned as examples herein, but should be considered in a broader sense within the spirit and scope of present invention. For a person skilled in the art it will be apparent that, for instance, the polyfunctional compound does not have to be a hydroxyl containing compound, but can also consist of other initiating species, such as, for example, amino groups.

**[0006]** In a preferred embodiment of the current invention a star-shaped copolymer or block copolymer of a lactide and one or more other cyclic esters, such as glycolide, trimethylene carbonate, lactones such as  $\beta$ -propiolactone,  $\delta$ -valerolactone,  $\epsilon$ -caprolactone, or lactones of larger size, or a mixture of two or more polymers, with at least one polymer

containing lactide, is used in the gum base. Preferably a system containing at least 50 mol % lactide, more particularly at least 65 mol % lactide, is used.

[0007] The polymerization can be done by any conventional polymerization technique, such as, for example, polymerization in bulk or solution, generally in the presence of a suitable polymerization catalyst.

[0008] A chewing gum typically consists of a water-soluble bulk part, a water-insoluble gum base, and flavoring components. The water-soluble part of the chewing gum comprises of, for example plasticizers, sweeteners and combinations thereof. Plasticizers, such as glycerin, lecithin and combinations thereof, are conventionally added for improving the softness and chewability of the water-insoluble gum base. It was, however, surprisingly noticed that in the current invention usage of plasticizers are not necessary in order to obtain the chewability and mouthfeel required in chewing gums. Plasticizers may optionally be used in the gum base formulations described herein.

[0009] The water-soluble sweeteners consists of, for example, saccharide containing components conventionally used in chewing gum, dried invert sugar, sucrose, dextrose, maltose, fructose, levulose, galactose and the like, alone or in combination with other sweeteners. Sugarless sweeteners, including, for instance, sugar alcohols such as sorbitol, mannitol, xylitol, maltitol, hydrogenated starch hydrolysates and the like, are also commonly used, alone or in combination with other sweeteners. Other typical sweeteners, such as, for example, aspartame, acesulfame, and saccharide, can be used alone or in combination.

[0010] A chewing gum can further contain about 0.1 to 10% flavoring components. The flavoring components may include, for example, oils from plants and fruits, such as citrus oil, fruit extracts, peppermint oil, spearmint oil, clove oil, aniseed oil, alone or as mixtures with other flavor inducing agents.

[0011] Furthermore, fillers, such as magnesium and calcium carbonate, kaolin, tricalcium phosphate, talc, wood fiber, apple fiber, zein, gluten, casein, can optionally be added to the chewing gum. Natural organic fillers are preferably used in current invention.

[0012] Additional components, such as colorants, medical components, mouth conditioners, and antioxidants, can also be added to the chewing gum, either during the polymerization or afterwards.

[0013] By no way of limiting the present invention, explanatory examples will be given in the following. The polymerization experiments were performed under an inert atmosphere in an electrically heated Brabender W 50 E mixer, unless otherwise stated. Usual polymerization conditions were as follows:

- Polymerization temperature: 140-170 °C
- Polymerization time: 30-240 min
- Rotationspeed of the mixer: 15 rpm
- 0.05 wt % stannous 2-ethylhexanoate was used as catalyst
- Amount of monomers and initiators were varied, depending on the calculated composition, so that total amount put in the mixer was 40 g

[0014] A GPC (Gel Permeation Chromatography) apparatus was used for molar mass measurements. The monomer conversion, number average molar mass, and copolymer composition were determined by NMR technique. Differential Scanning Calorimetry (DSC) was used for measuring the thermal properties, e.g. the glass transition temperature ( $T_g$ ).

[0015] While the invention has been described in detail with respect to specific preferred embodiments thereof, it will be appreciated that those skilled in the art, upon a reading and understanding of the foregoing will readily envision modifications and variations to the preferred embodiments which are nonetheless within the spirit and scope of the invention and of the claims.

#### EXAMPLE 1

[0016] An amorphous, non-crystallizable copolymer of (50/50)*rac*-lactide was prepared by ring-opening polymerization in the melt by using different hydroxyl compounds as initiators. The initiators and some polymer properties are listed in Table 1.

Table 1.

Examples on different initiators in the preparation of gum bases based on <i>rac</i> -lactide.				
Experiment No	Initiator	$M_w$ g/mol	$M_n$ g/mol	$T_g$ °C
1	1-decanol	33 500	20 000	44
2	Phloroglucinol	33 800	19 900	49
3	Inositol	16 400	12 600	44

Table 1. (continued)

Examples on different initiators in the preparation of gum bases based on <i>rac</i> -lactide.				
Experiment No	Initiator	M <sub>w</sub> g/mol	M <sub>n</sub> g/mol	T <sub>g</sub> °C
4	Dipentaerythritol	21 600	18 300	43

## EXAMPLE 2

[0017] Star-shaped copolymers of lactide and  $\epsilon$ -caprolactone were prepared by ring-opening polymerization in the melt by using a star-shaped poly( $\epsilon$ -caprolactone) with pentaerythritol core as macroinitiator. The star-shaped polymeric gum bases, with no components added, showed a chew feel similar to the one of a conventional commercially available chewing gum. The conditions during the experiments and the results from the series are shown in Table 2.

Table 2.

Examples on gum bases consisting of branched copolymers of lactide and $\epsilon$ -caprolactone.					
Experiment No	Lactide	$\epsilon$ -CL / Lactide ratio	M <sub>w</sub> g/mol	M <sub>n</sub> g/mol	T <sub>g</sub> °C
5	<i>Rac</i>	37 / 63	29 600	25 900	-20
6	L,L	42 / 58	26 400	23 900	- (*)
7	<i>Rac</i>	54 / 46	19 300	17 200 (**)	-23
8	<i>Rac</i>	32 / 68	43 700	32 600 (**)	-13
9	<i>Rac</i>	22 / 78	67 500	43 000 (**)	+2

\*) Not detected; DSC showed T<sub>m</sub> = 150 °C,  $\Delta H$  = 33 J/g

\*\*) Based on NMR

## EXAMPLE 3

[0018] Star-shaped random copolymers consisting of  $\epsilon$ -caprolactone and (50/50)*rac*-lactide was prepared by ring-opening polymerization, initiated by pentaerythritol, in the melt. The polymer characteristics are presented in Table 3.

Table 3.

Examples on gum bases consisting of branched random copolymers of <i>rac</i> -lactide and $\epsilon$ -caprolactone.				
Experiment No	$\epsilon$ -CL / Lactide ratio	M <sub>n</sub> g/mol (*)	M <sub>w</sub> / M <sub>n</sub>	T <sub>g</sub> °C
10	3 / 97	17 500	1.34	+46
11	8 / 92	16 700	1.35	+40
12	14 / 86	15 800	1.42	+35

\*) Based on NMR

## EXAMPLE 4

[0019] L-lactic acid was condensation polymerized in a rotavapor under reduced pressure and argon flow. The poly (lactic acid) (M<sub>n</sub> = 1 900 g/mol, MWD = 3.12) was further linked in the rotavapor with a star-shaped polycaprolactone with a pentaerythritol core, resulting in a star-shaped copolymer with M<sub>n</sub> = 7 400 g/mol. DSC showed a T<sub>g</sub> = -22 °C and T<sub>m</sub> = 130 °C.

## EXAMPLE 5

[0020] Star-shaped random copolymers consisting of  $\epsilon$ -caprolactone and (50/50) *rac*-lactide were prepared by ring-opening polymerization, initiated by pentaerythritol, in the melt. The amount of residual lactide available for hydrolysis (eventually into lactic acid) could be determined by the choice of polymerization time (Table 4).

Table 4.

The amount of residual lactide as a function of polymerization time.			
Experiment No (*)	Residual lactide at different polymerization times mol % (**)		
	30 min	60 min	90 min
10	7.0	5.6	3.6
11	10.7	3.9	2.7
12	4.3	2.4	1.8

\*) Experiment no. from Example 3

\*\*) Based on NMR

## Claims

1. Chewing gum, comprising a gum base and at least one other conventional chewing gum component, said chewing gum comprising as gum base at least one branched polymer mainly based on biodegradable and/or hydrolyzable ester groups.
2. Chewing gum, comprising a gum base and at least one chewing gum additive, said chewing gum comprising as chewing gum additives at least one branched polymer mainly based on biodegradable and/or hydrolyzable ester groups.
3. Chewing gum of claim 1 or 2, comprising as said at least one branched polymer a star-shaped biodegradable polymer with several branches or arms attached to a central polyfunctional compound.
4. Chewing gum of claim 3, wherein the said polyfunctional compound is based on one or more compounds having at least 3 hydroxyl or amino groups.
5. Chewing gum of claim 1, wherein the said at least one branched polymer is based on one or more cyclic esters (such as L,L-lactide, D,D-lactide, *rac*-lactide, *meso*-lactide,  $\epsilon$ -caprolactone, glycolide or rings of other size), cyclic carbonates (such as trimethylene carbonate), cyclic amides (such as caprolactam) by ring-opening polymerization.
6. Chewing gum of claim 5, wherein the said at least one branched polymer is made from one or more from one or more diol/diacid combinations, of from hydroxy acids, such as lactic acid and glycolic acid, or from amino acids by polycondensation.
7. Chewing gum compound of claim 1 where the starting compounds give the final formulation one or several functions, such as softening temperature, viscoelasticity, taste, compatibility or degradability.
8. Chewing gum compound of claim 1 where the processing conditions gives the final formulation one or several functions, such as softening temperature, viscoelasticity, taste, compatibility or degradability.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 01 20 1162

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D, X	EP 0 711 506 A (UNIV GRONINGEN) 15 May 1996 (1996-05-15) * the whole document *	1-8	A23G3/30
X	WO 00 19837 A (LI WEISHENG ; WRIGLEY W M JUN CO (US)) 13 April 2000 (2000-04-13) * the whole document *	1-8	
A	EP 0 882 751 A (KOBE STEEL EUROP LTD ; KOBE STEEL LTD (JP)) 9 December 1998 (1998-12-09) * the whole document *	1-8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			A23G
The present search report has been drawn up for all claims			
Place of search <b>MUNICH</b>		Date of completion of the search <b>7 August 2001</b>	Examiner <b>Weber, G</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.02 (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 20 1162

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-08-2001

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0711506	A	15-05-1996	NL	9401703 A	01-05-1996
			FI	954867 A	15-04-1996
			JP	8196214 A	06-08-1996
			US	5672367 A	30-09-1997
WO 0019837	A	13-04-2000	AU	9678298 A	26-04-2000
EP 0882751	A	09-12-1998	JP	11049851 A	23-02-1999
			US	5886093 A	23-03-1999

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82